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Mechanical properties of ladder-like polysilsesquioxane-based hard coating films containing different organic functional groups

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ABSTRACT

A series of ladder-like polysilsesquioxanes (LPSQs) containing the UV-curable methacryoxypropyl (MA) and different organic functional (R) groups (propyl, hexyl, cyclohexyl, phenyl or naphthyl) at the fixed MA/R molar ratio were synthesized as hard coating materials. The LPSQ hard coating films prepared by a simple UV curing process exhibited excellent optical transparency in the visible light range. X-ray diffraction analysis of the LPSQ films characterized how their intermolecular chain-to-chain distance and thus chain packing density varied according to the organic functional group. In addition, the hardness, elastic modulus and scratch resistance of the LPSQ films were evaluated by nanoindentation and nanoscratch tests. Although the mechanical properties of the LPSQ films were affected by both the chain rigidity of the organic functional group and the chain packing density of the siloxane backbones, chain rigidity played the dominant role in determining their mechanical robustness. Hence, despite its lowest chain packing density, the LPSQ film with the naphthyl group exhibited the best mechanical properties due to its high chain rigidity derived from the increased aromaticity of the naphthyl group. This study suggests the key factor when designing mechanically durable, scratch resistant hard coating films is the chain rigidity of the film network.

1. Introduction

Hard coating materials are widely used as protective films for displays, mobile phones, touch panels, DVDs, optical lenses and automobiles [1–6]. Their excellent mechanical properties, good optical transparencies and easy processabilities are desirable characteristics for hard coating materials. To date, a variety of organic polymer materials including polyacrylates, polyurethanes and polyesters have been developed as hard coating materials [7–9]. However, their inherently low mechanical robustness (*i.g.*, low hardness and poor scratch resistance) hindered their application as hard coating films. Recently, organic-inorganic hybrid materials have been extensively explored to overcome the limitations of organic materials and utilize the synergetic effects of organic and inorganic components [10]. Among them, silicon-based materials formed from organoalkoxysilane precursors have attracted great interest as hybrid hard coating materials because they make uniform hybrid structures at the molecular level and their chemical and mechanical properties can be effectively controlled by varying their organic functional groups [11,12].

Silsesquioxane, with the chemical formula $[SiO_{1.5}R]_n$, where R is an organic functional group, is one of silicon-based hybrid materials. It can be classified into random-branched silsesquioxane, cage-type polyhedral oligomeric silsesquioxane (POSS) and ladder-like structured polysilsesquioxane (LPSQ) depending on its siloxane (Si—O—Si) bonding structure [13]. Random-branched silsesquioxane typically has a large amount of uncondensed silanol (Si—OH) groups and thus may undergo undesirable structural shrinkage and/or cracking caused by the condensation reactions of the residual silanol groups during the thermal curing film fabrication process [14]. POSS, which has a nanometer-sized cage structure (1–3 nm in diameter), has been widely explored as an additive to polymeric materials to improve their mechanical and thermal stability [15]. However, its low molecular weight and poor solubility in common solvents has made its film formation challenging [16]. Unlike other silsesquioxanes, LPSQ is regarded as a promising candidate for the hard coating material due to its good mechanical properties, which are imparted by its unique double-stranded siloxane backbone structure [17,18]. Furthermore, its relatively high molecular weight combined with very scarce uncondensed silanol

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groups and good solubilities in a wide range of organic solvents, facilitates its formation of coating films [16,19]. In particular, when the UV-curable functional group is incorporated into LPSQ, the fabrication of a hard coating film with good mechanical robustness is enabled *via* a simple UV-curing process [20].

Previous works have focused on investigating how the mechanical properties of the LPSQ films are affected by varying the chemistry and composition of their organic functional groups. Two types of functional groups have been extensively explored: the phenyl group that confers high mechanical strength and curable groups, such as methacrylate [20], epoxy [21] and thiol [3,19], that confer curability, leading to the formation of mechanically robust, highly cross-linked LPSQ films. Previous studies have found that the mechanical properties of LPSQ films depend significantly on the chemistry and composition of functional groups [3,21]. However, the limited chemistries of organic functional groups (mainly the combination of the phenyl and curable groups) have been designed for these studies, limiting the achievable property spectrum of the LPSQ materials. In addition, the mechanical properties of LPSQ films have not been comprehensively correlated with their chain network structures depending on the organic functional group, which hampers our understanding of their structure-property relationship required for the rational design of hard coating films.

In this study, we synthesized a series of LPSQs containing the UV-curable methacryloxypropyl (MA) group and different organic functional (R) groups (propyl, hexyl, cyclohexyl, phenyl or naphthyl) at a fixed MA/R molar ratio (6:4) as hard coating materials. Varying the R groups allows us to understand the effects of their differing chemical structures, that is, the aliphatic carbon number (propyl *vs.* hexyl), cyclic *vs.* acyclic (hexyl *vs.* cyclohexyl), aliphatic *vs.* aromatic (cyclohexyl *vs.* phenyl) and the degree of aromaticity (phenyl *vs.* naphthyl), on the mechanical properties of the UV-cured LPSQ films. X-ray diffraction (XRD) analysis was employed to characterize the molecular network structure (*i.e.* intermolecular chain-to-chain distance and thus the chain packing density) of the LPSQ films. The mechanical properties of the LPSQ films were evaluated by nanoindentation and nanoscratch tests to determine the LPSQ structure most desirable for hard coating materials and to elucidate the LPSQ structure-property relationship.

2. Material and methods

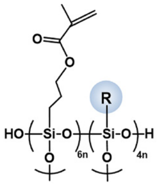
2.1. Materials

3-methacryloxypropyltrimethoxysilane (3-MPTS, Dynasylan® MEMO, Evonik), *n*-propyltrimethoxysilane (*n*-PTS, Dynasylan® PTMO, Evonik), hexyltrimethoxysilane (HTS, Gelest), cyclohexyltrimethoxysilane (CHTS, Gelest), phenyltrimethoxysilane (PTS, Dynasylan® 9165, Evonik,), 1-naphthyltrimethoxysilane (1-NTS, Gelest), tetrahydrofuran (THF, 99.9%, Sigma-Aldrich), dichloromethane (DCM, 99.5%, Daejung chemical), deuterated chloroform ($CDCl_3$, 99.8%, Sigma-Aldrich), anhydrous magnesium sulfate ($MgSO_4$, 99%, Daejung chemical) and Irgacure®184 (BASF) were used as purchased. Potassium carbonate (K_2CO_3, 99.5%, Daejung chemical) was dried in a vacuum oven at 40 °C overnight prior to use. Deionized (DI) water was prepared with the Millipore Milli-Q purification system.

2.2. Synthesis of LPSQs

The LPSQs containing MA and R groups (denoted as LMAR) were synthesized through the conventional hydrolysis and condensation reaction of organoalkoxysilane precursors in the presence of a base catalyst by following the previously reported method [20]. Briefly, to synthesize LPSQ containing MA and propyl (Pr) groups (LMAPr), a mixture of K_2CO_3 (0.04 g, 0.29 mmol), DI water (4.8 g, 0.267 mol) and THF (8 g) was prepared in a 100 mL round-bottomed flask. Next, 3-MPTS (11.92 g, 0.48 mol) and *n*-PTS (5.26 g, 0.32 mol) were added to the prepared mixture with purging nitrogen gas and vigorously stirred at room temperature for 48 h. Then, the mixture was separated into a colorless aqueous phase and a cloudy organic phase containing the product. After evaporation of the organic solvents from the organic phase, the remaining white viscous solution was dissolved in DCM and subsequently extracted with DI water three times. To remove the trace amount of water from the DCM solution, the drying agent $MgSO_4$ was added, stirred overnight and then filtered out. DCM was then evaporated off at 40 °C. Finally, LMAPr was obtained as a transparent oil-like product. The same synthesis protocol was employed, but replacing *n*-PTS with either HTS, CHTS, PTS or 1-NTS, to prepare LPSQs containing either hexyl (H), cyclohexyl (C), phenyl (P) or naphthyl (N) functional group, respectively, as well as the UV-curable MA group, as summarized in Table 1. The molar ratio of the MA group to the R group was fixed to 6:4 for all LMARs.

Table 1
The chemical structures of the synthesized LPSQs with the MA group and different organic functional R groups (LMARs).

LMAR	R group				
	Propyl [Pr]	Hexyl [H]	Cyclohexyl [C]	Phenyl [P]	Naphthyl [N]
					
	LMAPr	LMAH	LMAC	LMAP	LMAN

2.3. Fabrication of LPSQ films

The series of the synthesized LMARs were dissolved in THF (50 wt.%) containing a photo-initiator (Irgacure® 184, 1 wt.%) while shaking the mixtures for 1 h to prepare the transparent and viscous solutions. The solutions were cast on clean glass substrates and then dried at room temperature overnight, followed by further drying in a vacuum oven at 70 °C for 2 h to completely remove the residual solvent. The nascent LMAR films were irradiated with a UV-lamp system (365 nm, 5000-EC, Dymax Corp.) at a lamp intensity of 225 mW cm^{-2} for 10 min to obtain the fully cross-linked films, which were used in the subsequent characterizations. The thickness of all the prepared LMAR films was estimated to be 20 ± 2 μm.

2.4. Characterization of LPSQs and LPSQ films

Weight average molecular weight (M_w) and molecular weight distributions (M_w/M_n) of the synthesized LMARs were measured using a gel permeation chromatography (GPC) system equipped with an isocratic HPLC pump (1515, Waters), an autosampler injector (717 plus, Waters), a refractive index detector (2410, Waters) and styragel columns (HR 0.5, HR 2, HR 4, Waters) connected in line at a flow rate of 1 mL min^{-1} at 40 °C. Polystyrene (M_w: 1440; 2980; 7600; 20,300; 46,900; 120,000; 271,000; 715,000) was used as a standard material to calibrate the column. The synthesized LMARs were dissolved in $CDCl_3$ and their chemical structures were characterized using ^1H NMR (300 MHz, Varian Unity INOVA) and ^{29}Si NMR (99.5 MHz, Varian Unity INOVA). The chemical structures of the LMARs and their coating films were characterized using a Fourier transform infrared (FT-IR) spectrometer (Spectrum Two, PerkinElmer) with an attenuated total reflection unit in the wavenumber range from 750 to 4000 cm^{-1}. In addition, XRD spectra of the UV-cured LMAR films were collected to calculate the chain-to-chain distances of their siloxane backbones. XRD was performed on X-ray diffractometer (Smartlab, Rigaku) in the range of 2θ